



The
Patent
Office

FOI/00 38 / 026 / 1

09/508034

The Patent Office
Concept House
Cardiff Road
Newport
South Wales

| | |
|---------|-------------|
| NP9 TRH | 24 SEP 1998 |
| PCT | |

**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

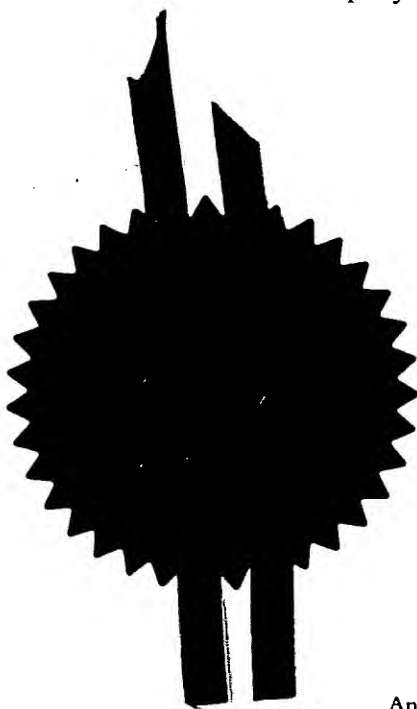
In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

Dated

15 SEP 1998



The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH**Request for grant of a patent***(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)*

1. Your reference **86999/PRS/VU**

2. Patent application number **9805478.6** **13 MAR 1998**
(The Patent Office will fill in this part)

3. Full name, address and postcode of the or of each applicant (underline all surnames)
**CAMBRIDGE DISPLAY TECHNOLOGY LTD
181A HUNTINGDON ROAD
CAMBRIDGE
CB3 0DJ**

Patents ADP number (if you know it)

6666441002

If the applicant is a corporate body, give the country/state of its incorporation

UNITED KINGDOM

4. Title of the invention **ELECTROLUMINESCENT DEVICES**

5. Name of your agent (if you have one)

PAGE WHITE & FARRER

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

**54 DOUGHTY STREET
LONDON
WC1N 2LS
UNITED KINGDOM**

Patents ADP number (if you know it)

1255003

If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body
See note (d))

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description 13
Claim(s) 5
Abstract 1
Drawing(s) 9 & 9

9

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77) 1

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature

Date

13 MARCH 1998

12. Name and daytime telephone number of person to contact in the United Kingdom

P R SLINGSBY

0171 831 7929

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

ELECTROLUMINESCENT DEVICES

This invention relates to electroluminescent devices, especially those that employ an organic material for light emission.

Electroluminescent devices that employ an organic material for light emission are described in PCT/WO90/13148 and US 4,539,507, the contents of both of which are incorporated herein by reference. The basic structure of these devices is a light-emissive organic layer, for instance a film of a poly(p-phenylenevinylene ("PPV"), sandwiched between two electrodes. One of the electrodes (the cathode) injects negative charge carriers (electrons) and the other electrode (the anode) injects positive charge carriers (holes). The electrons and holes combine in the organic layer generating photons. In PCT/WO90/13148 the organic light emissive material is a polymer. In US 4,539,507 the organic light emissive material is of the class known as small molecule materials, such as (8-hydroxyquinolino)aluminium ("Alq"). In a practical device, one of the electrodes is typically transparent, to allow the photons to escape the device.

As a preliminary point, it should be noted that the values stated here for energy levels, workfunctions etc. are generally illustrative rather than absolute. The workfunction of ITO can vary widely. Numbers quoted in the literature suggest a range between 4 and 5.2 eV. The 4.8 eV value used here serves as an illustrative rather than an absolute value. The applicant has carried out Kelvin probe measurements which suggest that 4.8 eV is a reasonable value. However, it is well known that the actual value can depend on ITO deposition process and history. For organic semiconductors important characteristics are the binding energies, measured with respect to the vacuum level of the electronic energy levels, particularly the "highest occupied molecular orbital" ("HOMO") and "lowest unoccupied molecular orbital" ("LUMO") levels. These can be estimated from measurements of photoemission and particularly measurements of the electrochemical potentials for oxidation and reduction. It is well understood in the

field that such energies are affected by a number of factors, such as the local environment near an interface, so the use of such values is indicative rather than quantitative.

These devices have great potential for displays. However, there are several significant problems. One is to make the device efficient, particularly as measured by its power efficiency and its external efficiency. Another is to reduce the voltage at which peak efficiency is obtained. Another is to stabilise the voltage characteristics of the device over time.

Figure 1 shows a cross section of a typical device. Figure 2 shows the energy levels across the device. The anode 1 is a layer of transparent indium-tin oxide ("ITO") with a workfunction of 4.8 eV. The cathode 2 is a CaAl layer of with a workfunction of 2.9 eV. Between the electrodes is a light emissive layer 3 of poly (2,7-(9,9-di-*n*-octylfluorene) ("F8") doped with 5% poly (2,7-(9,9-di-*n*-octylfluorene)-3,6-Benzothiadiazole) ("F8BT"), having a LUMO energy level 4 at around 2.8 eV and a HOMO energy level 5 at around 5.8 eV. (From now on the term "5F8BT" will be used to refer to the doped emissive layer blend). The dopant LUMO and HOMO levels are around 3.4 and 5.8 eV respectively. Holes and electrons that are injected into the device recombine radiatively in the 5F8BT layer. An important feature of the device is the hole transport layer 6 of polystyrene sulphonic acid doped polyethylene dioxythiophene ("PEDOT-PSS"). This provides an intermediate ionisation potential at around 4.8 eV, which helps the holes injected from the ITO to reach the HOMO level in the F8. However, there is still a large barrier (approximately 1.0 eV) between the hole transport layer and the light emissive layer, which results in the accumulation of holes. The accumulation of charge at an interface is undesirable, because this charge can promote chemical reactions between the polymer and contaminants. This can either lead to conjugation reduction or deep localised states that may then be charged by the accumulation layer. The net result from the charge "trapping" is that higher bias is required to pass the same current through the device. This leads to a relatively rapid voltage increase with time, as the device is used.

It is well-known to use oxygen plasma treatment to clean devices, and especially to remove organic material. It is also well known that such plasma treatment of ITO can be used to modify the ITO's work function and potentially reduce the hole injection barrier. (See, for example, WO 97/48115).

According to a first aspect of the present invention there is provided a method of forming an electroluminescent device, comprising: forming a first charge carrier injecting layer for injecting charge carriers of a first polarity; forming an organic charge carrier transport layer over the first charge carrier injecting layer, the transport layer having an ionisation potential for accepting charge carriers of the first polarity, which varies across the thickness of the transport layer; forming an organic light emissive layer over the transport layer; and forming a second charge carrier injecting layer over the light emissive layer for injecting charge carriers of a second polarity.

The step of forming a transport layer suitably comprises steps of first depositing the transport layer and then processing the transport layer to create the variation in the ionisation potential across the thickness of the transport layer. The ionisation potential may correspond to an energy level for accepting charge carriers of the first polarity or to an energy level for accepting charge carriers of the second polarity.

The charge carriers of a first polarity are suitably positive charge carriers, in which case the transport layer is a positive charge carrier transport layer.

According to a second aspect of the present invention there is provided a method of forming an electroluminescent device, comprising: forming a first charge carrier injecting layer for injecting positive charge carriers; forming an organic light emissive layer over the transport layer, the optical gap of the light emissive layer varying across the thickness of the emissive layer; and forming a second charge

carrier injecting layer over the light emissive layer for injecting negative charge carriers.

The step of forming a light emissive layer suitably comprises steps of first depositing the emissive layer and then processing the emissive layer to create the variation in the ionisation potential across its thickness.

The step of processing or modifying the emissive layer or, in the first aspect of the invention, the transport layer preferably comprises exposing the emissive or transport layer to an agent that causes modification of the electronic characteristics of the layer. One possibility is that the agent could be a reactive agent, which suitably promotes a chemical reaction in the transport layer. Preferably the conditions of the reaction are such that the degree of reaction varies through the emissive or transport layer so as to provide the variation in the ionisation potential. Preferably one major surface of the emissive or transport layer is exposed to the agent.

The reaction may suitably be an oxidation reaction and/or a de-doping reaction. The agent may be an oxidising agent, for example oxygen. The agent is suitably in the form of a plasma. One preferred reactive oxidising agent is an oxygen plasma. The degree of oxidation and/or de-doping preferably varies through the thickness of the transport layer or the emissive layer, suitably leading to the variation in the ionisation potential. The plasma preferably also comprises an inert gas, suitably for cooling purposes

The emissive or transport layer suitably comprises a conjugated material. Then, the step of creating the variation in the ionisation potential preferably comprises reducing the degree of conjugation of the conjugated material.

The ionisation potential preferably varies continuously or substantially continuously through the emissive or transport layer. In the first aspect of the invention, in a direction from the first charge carrier injecting layer to the light

emissive layer the ionisation potential preferably varies away from the conduction band of the first charge carrier injecting layer and/or towards the HOMO or LUMO level of the light emissive layer. In the second aspect of the invention the optical gap of the light emissive layer preferably widens in a direction from the first charge carrier injecting layer to the second charge carrier injecting layer.

According to a third aspect of the present invention there is provided an electroluminescent device comprising: a first charge carrier injecting layer for injecting positive charge carriers; a second charge carrier injecting layer for injecting negative charge carriers; an organic light emissive layer located between the charge carrier injecting layers; and an organic charge carrier transport layer located between the light emissive layer and one of the charge carrier injecting layers, and comprising an organic material having an ionisation potential for accepting positive charge carriers from the said one of the charge carrier injecting layers, which varies across the thickness of the transport layer.

According to a fourth aspect of the present invention there is provided an electroluminescent device comprising: a first charge carrier injecting layer for injecting positive charge carriers; a second charge carrier injecting layer for injecting negative charge carriers; and an organic light emissive layer located between the charge carrier injecting layers, the optical gap of the light emissive layer varying across the thickness of the emissive layer

According to a fifth aspect of the present invention there is provided a method of forming an electroluminescent device comprising a first charge carrier injecting layer for injecting charge carriers of a first polarity, a second charge carrier injecting layer for injecting charge carriers of a second polarity and at least one organic layer located between the charge carrier injecting layers, the method comprising partially oxidising the organic layer. The oxidation may, for example, be by exposure to a reactive oxidising agent such as an oxygen plasma or by photo-oxidation. Suitably a major surface of the transport layer or the light

emissive layer is exposed to the reactive oxidising agent or the light used for the photo-oxidation.

Some preferred materials for all aspects of the present invention are as follows:

- One of the charge carrier injecting layers (the hole injecting layer) preferably has a work function of greater than 4.3 eV. That layer may comprise ITO. The other charge carrier injecting layer (the electron injecting layer) preferably has a work function less than 3.5 eV. That layer may suitably comprise calcium, magnesium, aluminium or lithium or an alloy comprising one or more of those metals. At least one of the electrode layers is suitably light transmissive, and preferably transparent, suitably at the frequency of light emission from the device.
- The transport layer may suitably comprise one or more polymers such as polystyrene sulphonic acid doped polyethylene dioxythiophene and/or poly(2,7-(9,9-di-*n*-octylfluorene)-(1,4-phenylene-(4-imino(benzoic acid))-1,4-phenylene-(4-imino(benzoic acid))-1,4-phenylene)) ("BFA") and/or polyaniline and/or PPV.
- The light emissive layer may comprise one or more organic materials, suitably polymers, preferably conjugated or partially conjugated polymers. Suitable materials include PPV, poly(2-methoxy-5(2'-ethyl)hexyloxyphenylene-vinylene) ("MEH-PPV"), a PPV-derivative (e.g. a di-alkoxy or di-alkyl derivative), a polyfluorene and/or a co-polymer incorporating polyfluorene segments, PPVs and/or related co-polymers, poly(2,7-(9,9-di-*n*-octylfluorene)-(1,4-phenylene-((4-secbutylphenyl)imino)-1,4-phenylene)) ("TFB"), poly(2,7-(9,9-di-*n*-octylfluorene) - (1,4-phenylene-((4-methylphenyl)imino)-1,4-phenylene-((4-methylphenyl)imino) - 1,4-phenylene)) ("PFM"), poly(2,7 - (9,9 - di-*n*-octylfluorene) - (1,4-phenylene-((4-methoxyphenyl)imino)-1,4-phenylene- ((4-methoxyphenyl)imino)-1,4-phenylene)) ("PFMO"), F8 or F8BT. Alternative materials include organic molecular light-emitting materials, e.g. Alq, or any other small sublimed molecule or conjugated polymer electroluminescent material as known in the prior art.

Other materials could be used.

The effect of the variation in the ionisation potential of the transport layer and/or the step of modifying the transport layer by (for example) oxidation is suitably to improve transport of the charge carriers across the transport layer and thereby improve the efficiency of the device. The effect of the variation in the optical gap of the emissive layer is preferably to inhibit passage of charge carriers of at least one polarity through the emissive layer and collection by the opposite charge injecting layer.

The present invention will now be described by way of example with reference to the accompanying drawings, in which:

figure 3 shows the chemical structures of PEDOT-PSS, F8 and F8BT;

figure 4 is a schematic band diagram for an electroluminescent device;

figures 5 to 9 are graphs plotting the performance of electroluminescent devices;

figure 10 illustrates the effect of plasma on an emissive layer adjacent to a cathode; and

figure 11 illustrates a device in which photo-oxidation alters the electronic characteristics of a PPV hole transport layer.

Figure 4 shows a schematic band diagram for an electroluminescent device whose physical structure is similar to that shown in figure 1. The device comprises an anode layer 10 of ITO on a glass substrate. Over the ITO is a hole transport layer 11 of PEDOT-PSS. Over the hole transport layer is a light emissive layer 12 comprising a mixture of F8 and F8BT. Over the light emissive layer is a cathode layer 13 of CaAl. The ionisation potential of the PEDOT-PSS is not constant through the thickness of the hole transport layer 11. It ranges from the normal level of 4.8 eV near the interface with the anode 10 to possibly up to 6.0 eV at the interface with the light emissive layer 12. The applicant has found that this spatial variation in the ionisation potential appears to improve the performance of the device dramatically.

The manufacture of this device will now be described.

The glass substrate is a polished glass sheet of sodalime glass 1.1mm thick, with a barrier layer of silicon dioxide around 100nm thick on its upper surface. The ITO anode is deposited on to the silicon dioxide by a conventional DC or RF sputtering technique. The completed ITO layer is about 1500Å thick with a sheet resistance of around 15 Ohm/square and a transparency of about 85%. Alternatives to ITO are other conductive materials such as fluorine-doped tin-oxide, aluminium-doped zinc-oxide, metals such as gold, alloys and conductive polymers such as PEDOT-PSS or doped polyaniline, or combinations thereof. To provide an effective anode the material is preferably a high work function material, with a work function higher than, say, 4.0 or 4.5eV. In devices where the emitted light is to be transmitted through the anode, the anode should be at least partially transparent or light transmissive.

At this stage the ITO layer can, if necessary, be patterned, for example by conventional wet-chemical ITO patterning techniques, and then cleaned.

The PEDOT-PSS is a conductive conjugated polymer layer. The PEDOT-PSS mixture is prepared (see EP 0 686 662 and Bayer AG's Provisional Product Information Sheet for Trial Product AI 4071) with a ratio of PEDOT to PSS of 1:2 and a solid content of 1%. The mixture is deposited on to the ITO layer by spin coating and then cured by heating - for instance at 110°C or 200°C in air or flowing nitrogen of purity 99.999%. Then the PEDOT-PSS layer is exposed to a reactive agent, more details of which are given below. The thickness of the completed PEDT/PSS layer is around 50nm.

To prepare the emissive layer the precursors of F8 and F8BT are mixed (the ratio of F8 to F8BT is 0.95:0.05) and the resulting mixture is then spin-coated over the PEDOT-PSS layer from a 1.6% concentration solution with mixed xylene as the solvent. The thickness of the completed emissive layer is around 95nm. Table 1 gives material properties of the conjugated organic polymer materials F8 and

F8BT. The photoluminescence efficiencies were measured using the technique of "Efficient Photodiodes from Interpenetrating Polymer Networks", J J M Halls et al., Nature, Vol. 376, 10 August 1995, pp498-500 and US 5,670,791. The HOMO positions were estimated from electrochemical measurement. The optical gaps were determined from the UV/visible absorbance spectrum. The LUMO positions were estimated from the HOMO position and the optical gap.

Table 1

| Material | Photoluminescence Efficiency (%) | HOMO Level (eV) | LUMO Level (eV) | Optical gap (eV) | Emission Colour |
|----------|-------------------------------------|--------------------|--------------------|---------------------|--------------------|
| F8 | 80 | 5.8 | 2.8 | 3.0 | Blue |
| F8BT | 95 | 5.9 | 3.5 | 2.4 | Green |

Finally the cathode is deposited by evaporation to form a 80nm thick layer of Ca, followed by a 200nm layer of Al. In an inert atmosphere such as nitrogen the device is encapsulated by sealing within a glass/epoxy encapsulant.

The reactive treatment of the PEDOT-PSS layer will now be described. After the PEDOT-PSS layer has been deposited and cured it is exposed to reactive oxygen in the form of an oxygen plasma. The oxygen plasma is generated by a standard commercial microwave multimode plasma reactor such as a Cambridge Fluid Systems MRC100 (2.45GHz) under the following process conditions:

chamber pressure: 2 mB
 argon flow: 5 l/min
 oxygen flow: 2 l/min
 power: high (0.044 w/cm²)
 ion density: 10¹²/cm²
 electron temp.: 1-2 eV
 ion flux: 4x10¹⁵ - 4x10¹⁶ ion/cm²/sec

Argon is added to the plasma to cool the substrate. It is the major surface of the PEDOT-PSS that is to form the interface with the emissive layer that is principally

exposed to the plasma. Therefore, the oxidising effect of the plasma is greatest at that surface and decreases with depth into the PEDOT-PSS layer as the penetration of excited oxygen is likely to be shallow and will depend on ion energy. The plasma is applied to the device for sufficient time that the PEDOT-PSS does not react fully with the oxygen, at least at deeper parts of the layer (i.e. those closer to the anode). This produces the effect shown in figure 4, where the energy level of the PEDOT-PSS varies smoothly and continuously through the thickness of the layer when the device is not under external bias, from its normal level near the interface with the anode to a reduced level closer to the HOMO level of the emissive layer near the interface with the emissive layer.

Using a plasma source where the ion energy can be controlled (e.g. via a bias voltage), the ion flux monitored and the ratio of ions to radicals selected makes it easier to select the shape and extent of the transition region from the normal doped PEDOT workfunction (W_t) to the surface workfunction (W_s). The transition region can be controlled so that the effective surface workfunction can be tuned approximately to the HOMO position of the emissive polymer. Further, if essentially a thin oxide layer was required then modifying the plasma so that only radicals impinged the surface would have the desired effect.

Devices A to D were prepared, with different treatments being applied to the PEDOT-PSS layers.

For device A the PEDOT-PSS layer was cured in an oven for 1 hour in a N_2 atmosphere at 200°C and then exposed to oxygen plasma for 20 seconds. For device B the PEDOT-PSS layer was cured in an oven for 1 hour in a N_2 atmosphere at 200°C and then exposed to oxygen plasma for 1 minute. Devices C and D were prepared as controls. For device C the PEDOT-PSS layer was cured in an oven for 1 hour in a N_2 atmosphere at 200°C and not exposed to plasma. For device D the PEDOT-PSS layer was cured on a hot plate for 1 hour in air, with the hot plate at a temperature of 200°C, and not exposed to plasma.

Figures 5 to 9 compare the performance of these devices. Figures 5 to 8 show the characteristics of devices A to D respectively. The top panel of each figure shows the brightness of the device against applied voltage and the current density through the device against applied voltage. The bottom panel of each figure shows the luminous efficiency (power efficiency) of the device against applied voltage and external efficiency of the device against applied voltage.

The following table summarises the performance of the devices from the data of figures 5 to 8.

Table 2

| Device | Peak power efficiency (lm/W) | Voltage at peak power efficiency (V) | Peak external efficiency (Cd/A) | Voltage at peak external efficiency (V) |
|--------|------------------------------|--------------------------------------|---------------------------------|---|
| A | 5.6 | 3.8 | 6.7 | 3.8 |
| B | 6.1 | 3.6 | 7.0 | 3.6 |
| C | 2.4 | 6.8 | 5.5 | 8 |
| D | 2.0 | 7.0 | 4.9 | 8.4 |

The step of exposure of the PEDOT-PSS layer to oxygen plasma appears to cause roughly a three-fold increase in the peak power efficiency and a significant increase in peak external efficiency. The voltages at which peak efficiencies are obtained are roughly halved.

Figure 9 shows that exposure of the PEDOT-PSS layer to oxygen plasma also appears to stabilise the voltage characteristics of the device significantly for an initial light output of 200 Cd/m².

One possible mechanism for the effect of the oxygen plasma on the PEDOT-PSS is oxidation of the PEDOT-PSS layer, possibly by producing carbonyl groups which reduce conjugation in the PEDOT-PSS and widen its band gap (see Rothberg et al., "Photophysics of phenylenevinylene polymers", Synthetic Metals

80 (1996) 41-58). Another possible mechanism is that the oxygen plasma could de-dope the PEDOT-PSS, shortening polymer sequences on the polymer chain, and thus increase its work function. In either case, it would appear that the HOMO level of the PEDOT-PSS may be bent to be closer to that of the emissive layer near the interface between the two, as shown in figure 4. The reduced voltage increase with time suggests that the HOMO level transition from the doped value of 4.8 eV to the surface value must be gradual through the thickness of the PEDOT-PSS layer.

A similar technique may be used to widen the bandgap of material forming a light emissive layer. (See figure 10). By exposing a light emissive layer, after it has been deposited, to (for example) oxygen plasma the HOMO layer of the emissive material (e.g. PPV) may be reduced near its surface that is to form the interface with the cathode. This may inhibit passage of holes from the emissive material to the cathode, increasing the efficiency of the device. Another option is to photo-oxidise the PPV to create carbonyl groups (see Rothberg et al., referred to above, and Harrison et al., "Singlet Intrachain Exciton Generation and Decay in Poly(p-phenylenevinylene)", *Physical Review Letters*, Vol. 77, No. 9, pp 1881-4, 22 August 1996). With above optical-gap enhanced photo-oxidation, the wavelength of the light used for the oxidation step may be chosen for absorption depth to achieve the desired depth profile of ionisation potential, because the process may not be limited by the oxygen diffusion rate. However, the best wavelength may be near to the peak in optical absorption of the layer (blue for PPV). Chain scission on photo-oxidation of PPV is likely to force a greater change in E_A than in I_P , widening the optical gap of the PPV. (See figure 11, which illustrates the case where PPV is used as a hole injection layer and 5F8BT is the emitting layer).

Hydrogen plasma instead of oxygen plasma could be used, potentially with the opposite effect on ionisation energies.

Alternative materials could be used in devices that embody the principles described above. For example, alternative materials for the anode include tin

oxide ("TO") and fluorinated TO; alternative materials for the emissive layer include TFB, PFMO, PFM, PPV and MEH-PPV; and alternative materials for the cathode include Ca, Yb, Li, Sm and Tb and alloys containing at least one low-workfunction (e.g. LiAl) material. The cathode could be transparent. The hole transport layer could be omitted, or there could be more than one hole transport layer. There could be one or more electron transport layers between the cathode and the emissive layer, which would act to facilitate transfer of electrons from the cathode to the emissive layer and/or to block passage of holes to the cathode.

Instead of PEDOT-PSS the hole transport layer could comprise BFA or polyaniline. The hole transport layer could be a mixture of materials. For instance, it could be of BFA blended with a PFM-like polymer but with solution solvency as for the BFA adjusted by the inclusion of carboxylic acid groups.

Other oxidising agents could be used. One option is to use exposure to hydrogen peroxide. Treatments that reduce the effect of PSS on PEDOT, such as ammonia, could also be considered.

The present invention may include any feature or combination of features disclosed herein either implicitly or explicitly or any generalisation thereof irrespective of whether it relates to the presently claimed invention. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

CLAIMS

1. A method of forming an electroluminescent device, comprising:
 - forming a first charge carrier injecting layer for injecting charge carriers of a first polarity;
 - forming an organic charge carrier transport layer over the first charge carrier injecting layer, the transport layer having an ionisation potential which varies across the thickness of the transport layer;
 - forming an organic light emissive layer over the transport layer; and
 - forming a second charge carrier injecting layer over the light emissive layer for injecting charge carriers of a second polarity.
2. A method as claimed in claim 1, wherein the step of forming a transport layer comprises the steps of depositing the transport layer and processing the transport layer to create the spatial variation in the ionisation potential.
3. A method as claimed in claim 2, wherein the transport layer comprises a conjugated material and the step of creating the variation in the ionisation potential comprises reducing the degree of conjugation of the conjugated material.
4. A method as claimed in claim 2 or 3, wherein the step of processing the transport layer comprises exposing the transport layer to a reactive agent to promote a chemical reaction in the transport layer.
5. A method as claimed in claim 4, wherein the reaction is an oxidation reaction and/or a de-doping reaction.
6. A method as claimed in claim 4 or 5, wherein the reactive agent is an oxidising agent.
7. A method as claimed in any of claims 4 to 6, wherein the agent is oxygen.

8. A method as claimed in any of claims 4 to 7, wherein the agent is in the form of a plasma.

9. A method as claimed in any preceding claim, wherein in a direction from the first charge carrier injecting layer to the light emissive layer the ionisation potential varies away from the conduction band of the first charge carrier injecting layer.

10. A method as claimed in any preceding claim, wherein the charge carriers of a first polarity are positive charge carriers.

11. A method as claimed in any preceding claim, wherein in a direction from the first charge carrier injecting layer to the light emissive layer the ionisation potential varies towards the HOMO level of the light emissive layer.

12. A method as claimed in any preceding claim, wherein the transport layer comprises polystyrene sulphonic acid doped polyethylene dioxythiophene and/or BFA and/or polyaniline and/or PPV.

13. A method of forming an electroluminescent device, comprising:

forming a first charge carrier injecting layer for injecting positive charge carriers;

forming an organic light emissive layer over the transport layer, the optical gap of the light emissive layer varying across the thickness of the emissive layer; and

forming a second charge carrier injecting layer over the light emissive layer for injecting negative charge carriers.

14. A method as claimed in claim 13, wherein the step of forming a light emissive layer comprises the steps of depositing the emissive layer and processing the emissive layer to create the variation in the optical gap across the thickness of the emissive layer.

15. A method as claimed in claim 13 or 14, wherein the emissive layer comprises a conjugated material and the step of creating the variation in the ionisation potential comprises reducing the degree of conjugation of the conjugated material.
16. A method as claimed in claim 14 or 15, wherein the step of processing the transport layer comprises exposing the transport layer to a reactive agent to promote a chemical reaction in the transport layer.
-
17. A method as claimed in claim 16, wherein the reaction is an oxidation reaction and/or a de-doping reaction.
18. A method as claimed in claim 16 or 17, wherein the reactive agent is an oxidising agent.
19. A method as claimed in any of claims 16 to 18, wherein the agent is oxygen.
20. A method as claimed in any of claims 16 to 19, wherein the agent is in the form of a plasma.
21. A method as claimed in any preceding claim, wherein the optical gap of the light emissive layer widens in a direction from the first charge carrier injecting layer to the second charge carrier injecting layer.
22. A method of forming an electroluminescent device comprising a first charge carrier injecting layer for injecting charge carriers of a first polarity, a second charge carrier injecting layer for injecting charge carriers of a second polarity and at least one organic layer located between the charge carrier injecting layers, the method comprising partially oxidising the organic layer.
23. A method as claimed in claim 22, wherein the organic layer is a charge transport layer.

24. A method as claimed in claim 22, wherein the organic layer is a light emissive layer.

25. A method as claimed in any of claims 22 to 24, wherein the step of oxidising the organic layer comprises exposing the organic layer to an oxidising agent.

26. A method as claimed in claim 25, wherein the oxidising agent is a reactive oxidising agent.

27. A method as claimed in claim 26, wherein the oxidising agent is an oxygen plasma.

28. A method as claimed in any of claims 22 to 27, wherein the step of oxidising the organic layer comprises exposing the organic layer to light to perform a photo-oxidisation process.

29. A method as claimed in any of claims 25 to 28, wherein the or each step of exposing comprises exposing a major surface of the organic layer.

30. A method as claimed in any of claims 22 to 29, wherein the step of partially oxidising the organic layer comprises creating a gradation of oxidation through at least part of the thickness of the layer.

31. A method as claimed in claim 30, wherein the gradation of oxidation results in a gradation of ionisation potential.

32. A method as claimed in claim 31, wherein the ionisation potential corresponds to an energy level for accepting positive charge carriers.

33. A method as claimed in claim 31, wherein the ionisation potential corresponds to an energy level for accepting negative charge carriers.

34. An electroluminescent device comprising:

- a first charge carrier injecting layer for injecting positive charge carriers;
- a second charge carrier injecting layer for injecting negative charge carriers;
- an organic light emissive layer located between the charge carrier injecting layers; and

an organic charge carrier transport layer located between the light emissive layer and one of the charge carrier injecting layers, and comprising an organic material having an ionisation potential for accepting positive charge carriers from the said one of the charge carrier injecting layers, which varies across the thickness of the transport layer.

35. An electroluminescent device comprising:

- a first charge carrier injecting layer for injecting positive charge carriers;
- a second charge carrier injecting layer for injecting negative charge carriers; and
- an organic light emissive layer located between the charge carrier injecting layers, the optical gap of the light emissive layer varying across the thickness of the emissive layer

36. A method of forming an electroluminescent device substantially as herein as described with reference to figures 3 to 10 of the accompanying drawings.

37. An electroluminescent device substantially as herein as described with reference to figures 3 to 10 of the accompanying drawings.

ABSTRACT**ELECTROLUMINESCENT DEVICES**

A method of forming an electroluminescent device, comprising: forming a first charge carrier injecting layer for injecting charge carriers of a first polarity; forming an organic charge carrier transport layer over the first charge carrier injecting layer, the transport layer having an ionisation potential for accepting charge carriers of the first polarity, which varies across the thickness of the transport layer; forming an organic light emissive layer over the transport layer; and forming a second charge carrier injecting layer over the light emissive layer for injecting charge carriers of a second polarity.

Figure 4

1/9

Fig. 1

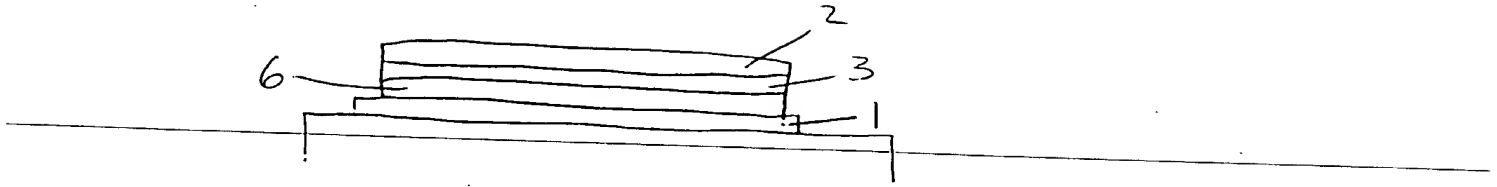


Fig. 2

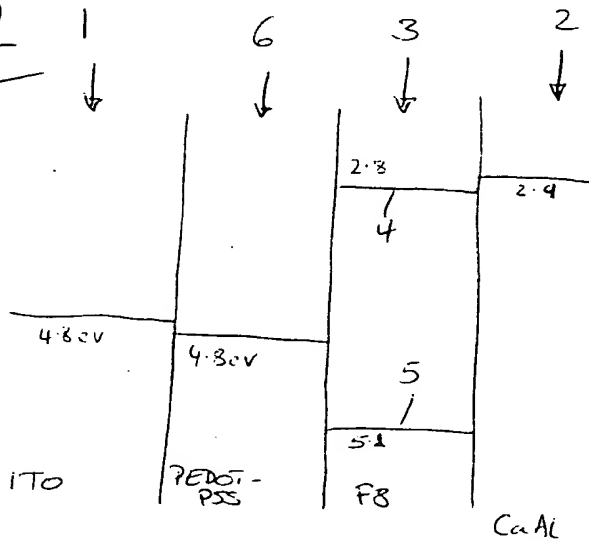


Fig. 4

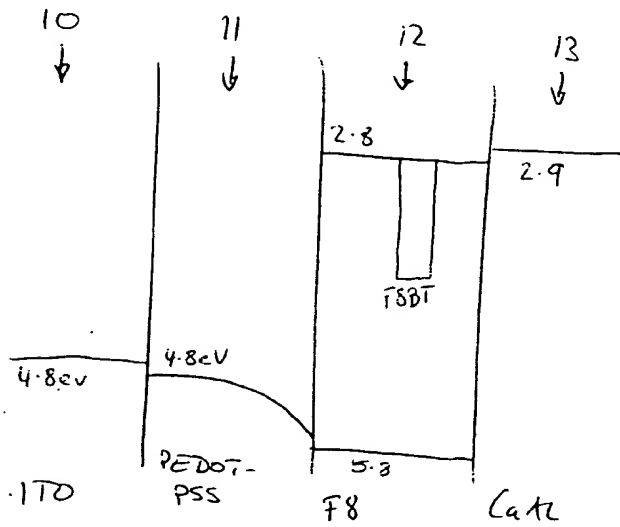
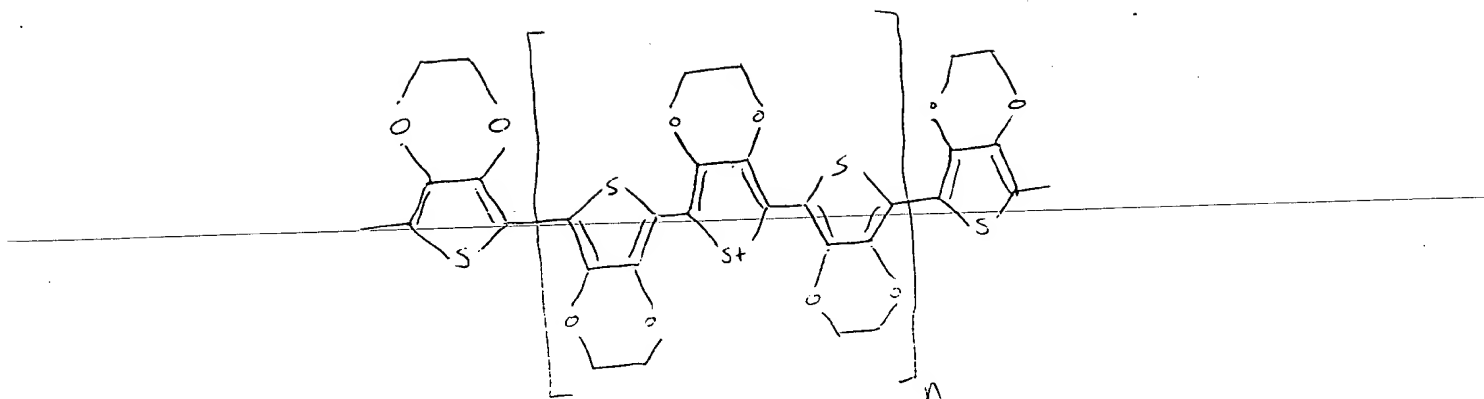
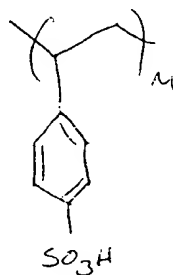
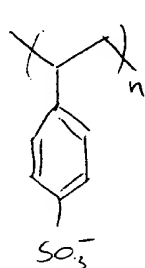


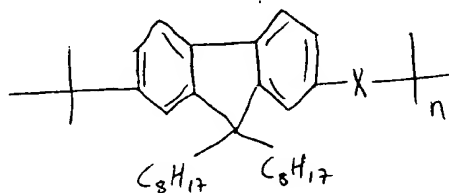
Fig. 3



PEDOT-PSS



F8



F8BT

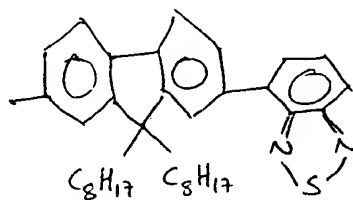
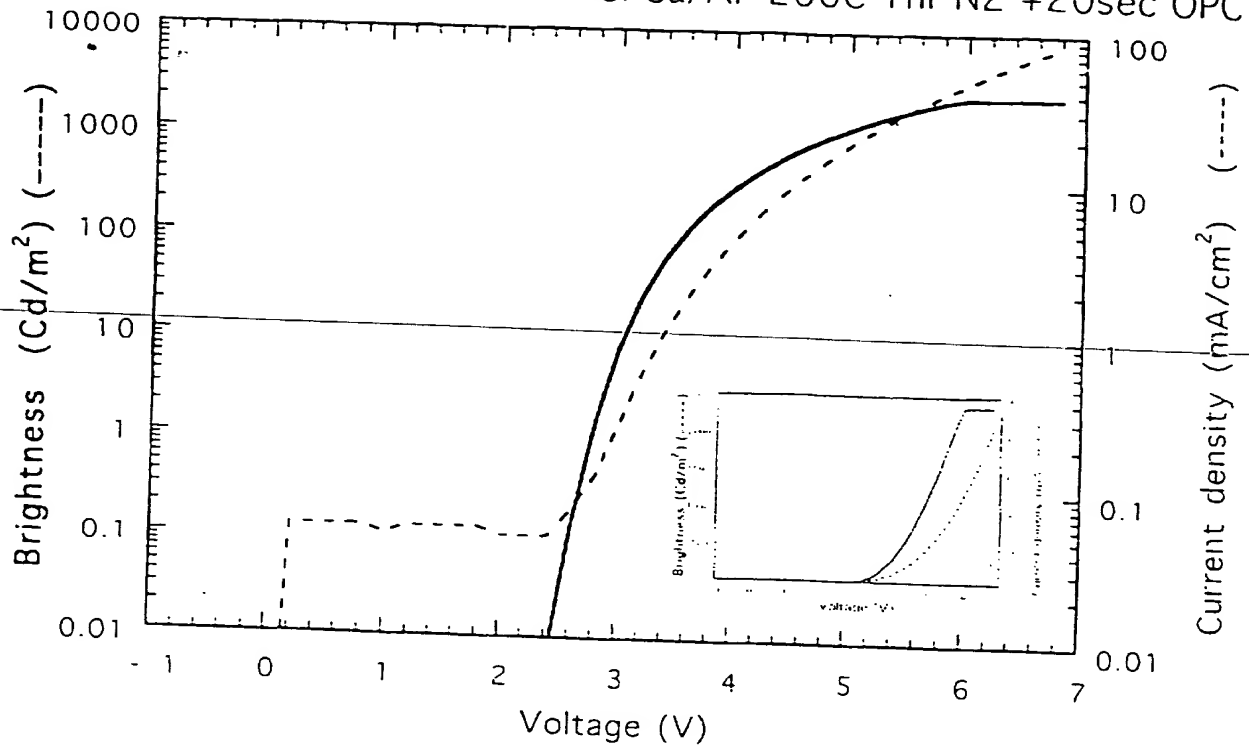


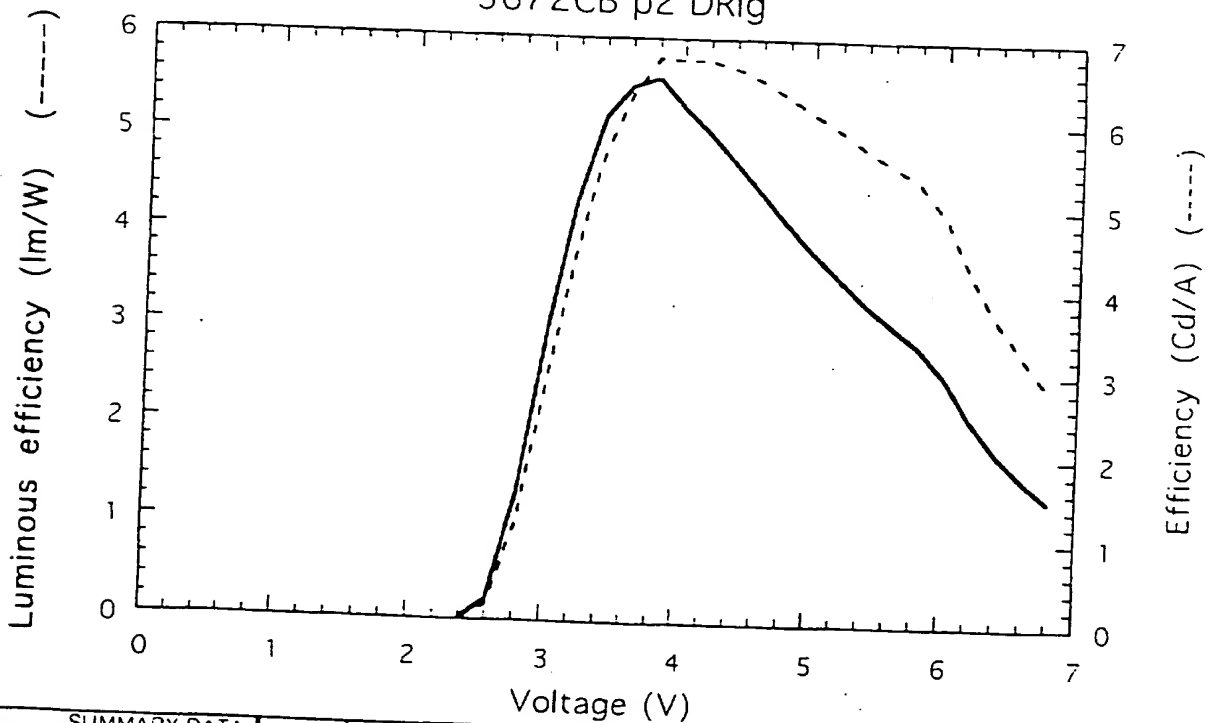
Fig. 5

3/9

1:1.5 /5BTF8/Ca/Al 200C 1hr N2 +20sec OPC



5672CB p2 DRig

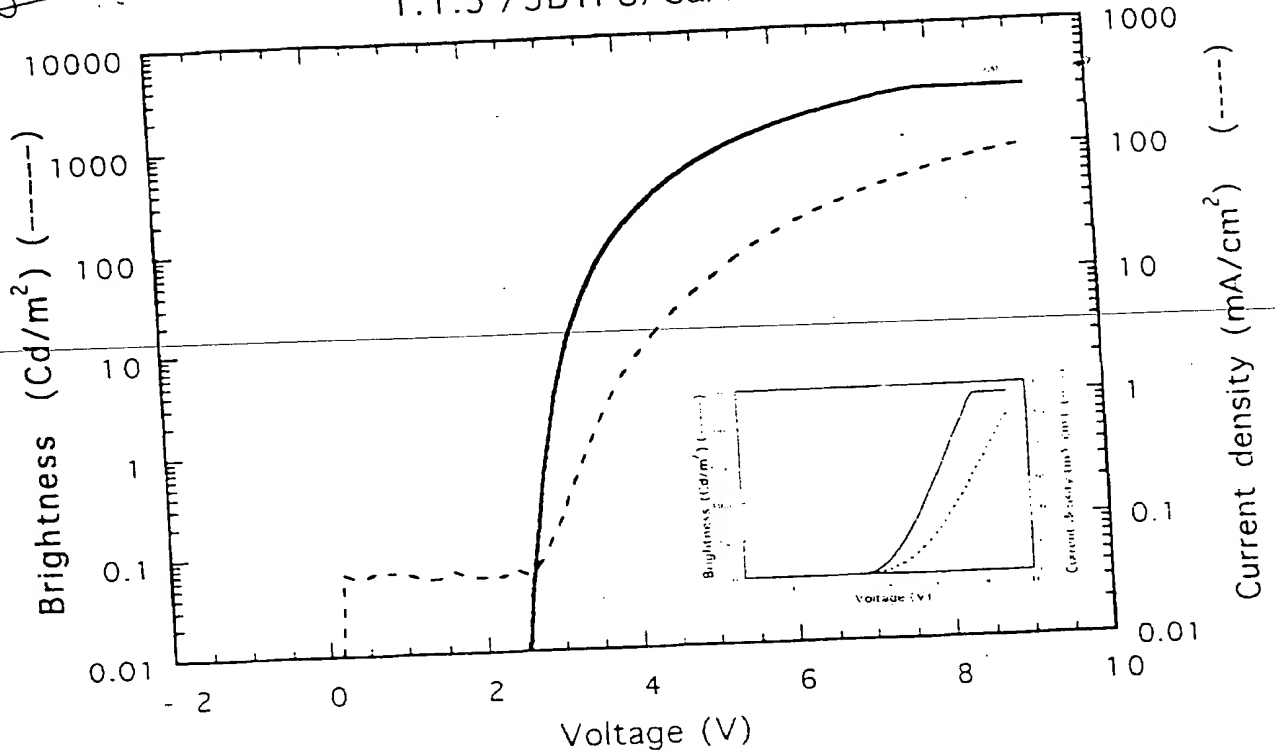


| SUMMARY DATA | | | | | |
|-----------------------|--------|-----------------------|--------|-----------------------|--------|
| Lumens/W @ 60 mA/sq | 1.9877 | Cd/A @ 60 mA/sq | 3.9754 | Final lm/W | 1.3009 |
| Max lm/W | 5.5935 | Max Cd/A | 6.7692 | Final Cd/A | 2.8173 |
| L(Cd/sqm) @ max lm | 202.67 | L(Cd/sqm) @ max Cd/A | 202.67 | Final Light (Cd/sqm) | 2372.9 |
| I (mA/sq cm) @ max lm | 2.9940 | I (mA/sq cm) @ max Cd | 2.9940 | Final Current (mA/sq) | 84.228 |
| Volts (V) @ max lm | 3.8000 | Volts (V) @ max Cd/A | 3.8000 | Final Voltage (V) | 6.8000 |
| Volts (V) @ 0.01 Cd/s | 2.4082 | Volts (V) @ 30 Cd/Sqm | 3.2274 | Volts (V) @ 100 Cd/Sq | 3.5380 |

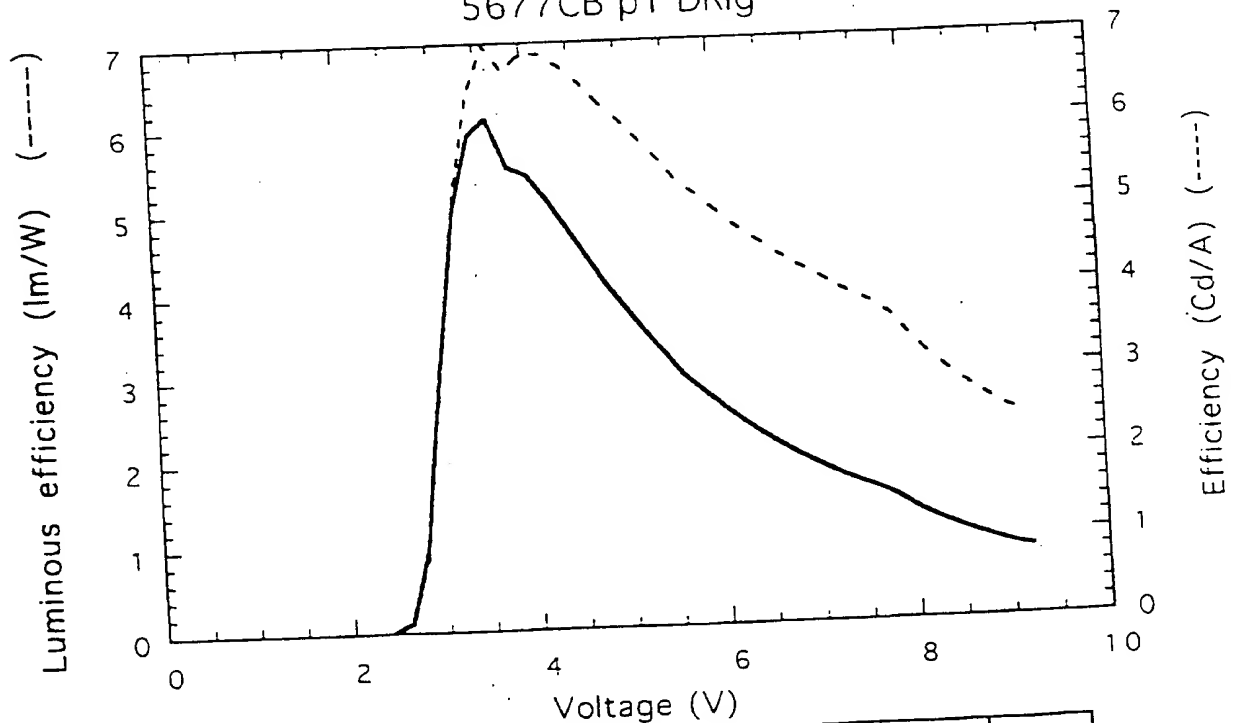
4/9

Fig. 6

1:1.5 / 5BTF8/Ca/Al 200C N2 + 1 min OPC



5677CB p1 DRig

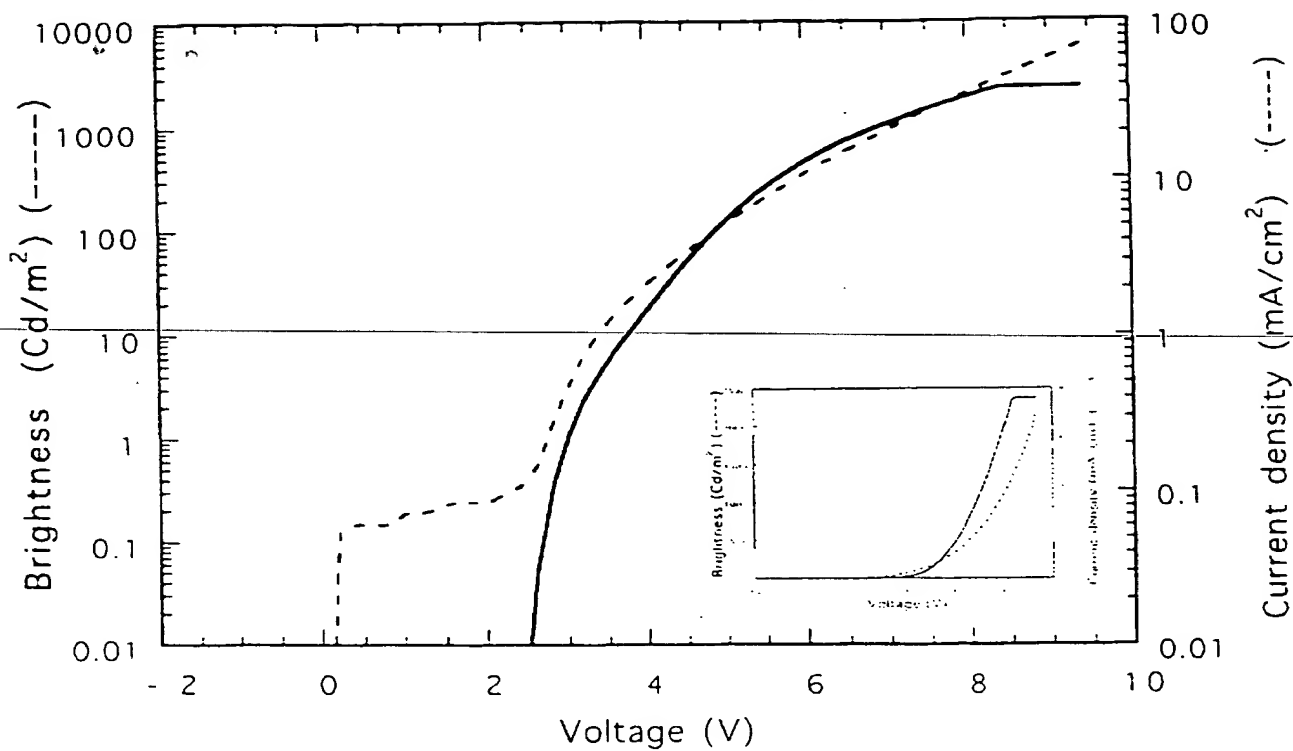


| SUMMARY DATA | | | | | |
|----------------------|---------|----------------------|---------|-----------------------|---------|
| Lumens/W @ 60 mA/sq | 1.5670 | Cd/A @ 60 mA/sq | 3.7914 | Final lm/W | 0.80983 |
| Max lm/W | 6.0985 | Max Cd/A | 6.9919 | Final Cd/A | 2.3727 |
| L(Cd/sqm)@max lm | 60.829 | L(Cd/sqm)@max Cd/A | 60.829 | Final Light (Cd/sqm) | 2373.2 |
| I (mA/sq cm) @max lm | 0.87000 | I (mA/sq cm) @max Cd | 0.87000 | Final Current (mA/sq) | 100.02 |
| Volts (V)@max lm | 3.6000 | Volts (V)@max Cd/A | 3.6000 | Final Voltage (V) | 9.2000 |
| Volts (V)@ 0.01 Cd/s | 2.4479 | Volts (V)@ 30 Cd/Sqm | 3.3888 | Volts (V)@ 100 Cd/Sq | 3.7927 |

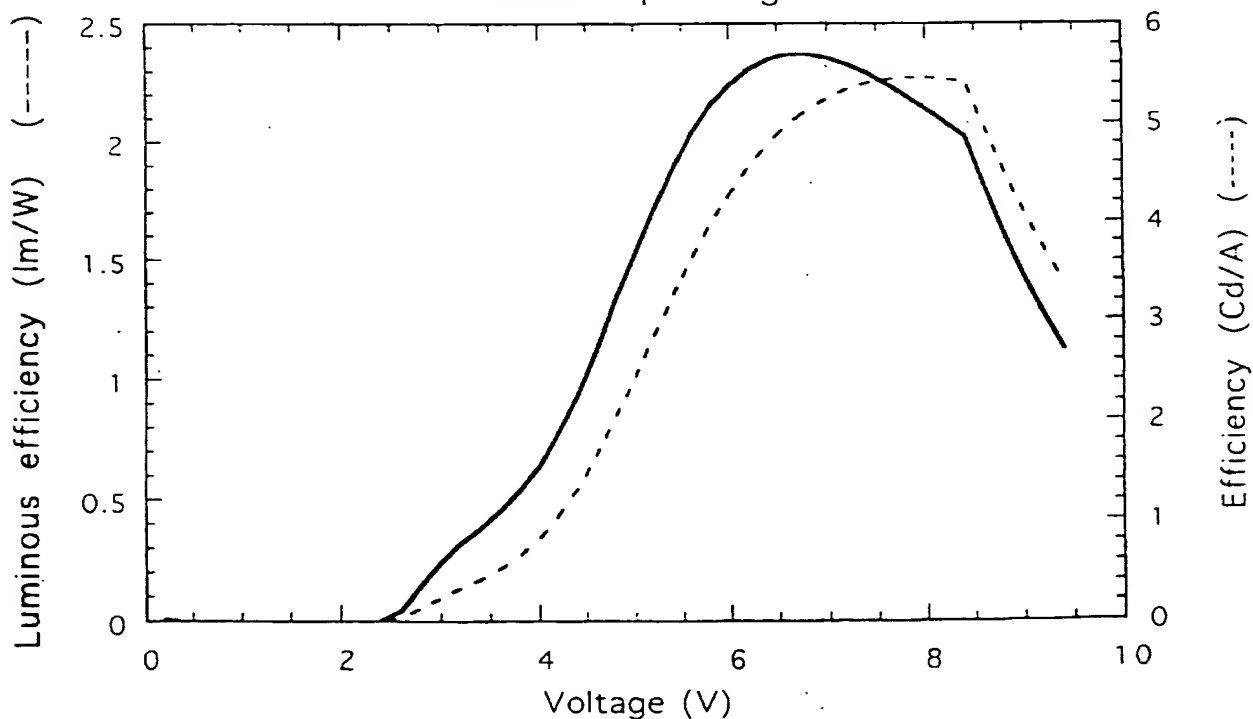
Fig. 7

5/9

1:1.5 /5BTf8/Ca/Al 200C N2 1hr



5665CB p2 DRig

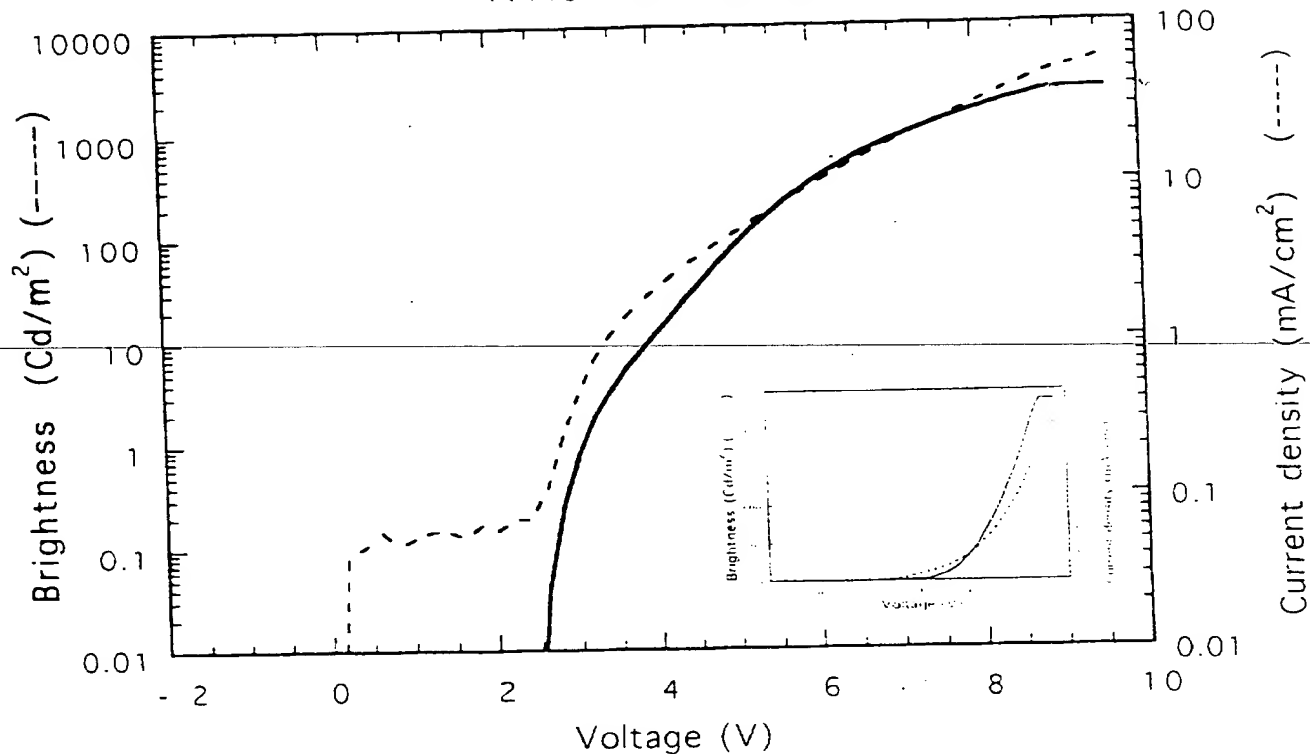


| SUMMARY DATA | | | | | |
|----------------------|--------|----------------------|--------|-----------------------|--------|
| Lumens/W @ 60 mA/sq | 1.3736 | Cd/A @ 60 mA/sq | 3.9633 | Final lm/W | 1.1251 |
| Max lm/W | 2.3722 | Max Cd/A | 5.4572 | Final Cd/A | 3.3681 |
| L(Cd/sqm)@max lm | 927.49 | L(Cd/sqm)@max Cd/A | 1928.9 | Final Light (Cd/sqm) | 2373.3 |
| I (mA/sq cm) @max lm | 18.054 | I (mA/sq cm) @max Cd | 35.346 | Final Current (mA/sq) | 70.464 |
| Volts (V)@max lm | 6.8000 | Volts (V)@max Cd/A | 8.0000 | Final Voltage (V) | 9.4000 |
| Volts (V)@ 0.01 Cd/s | 2.4330 | Volts (V)@ 30 Cd/Sqm | 4.2429 | Volts (V)@ 100 Cd/Sq | 4.8594 |

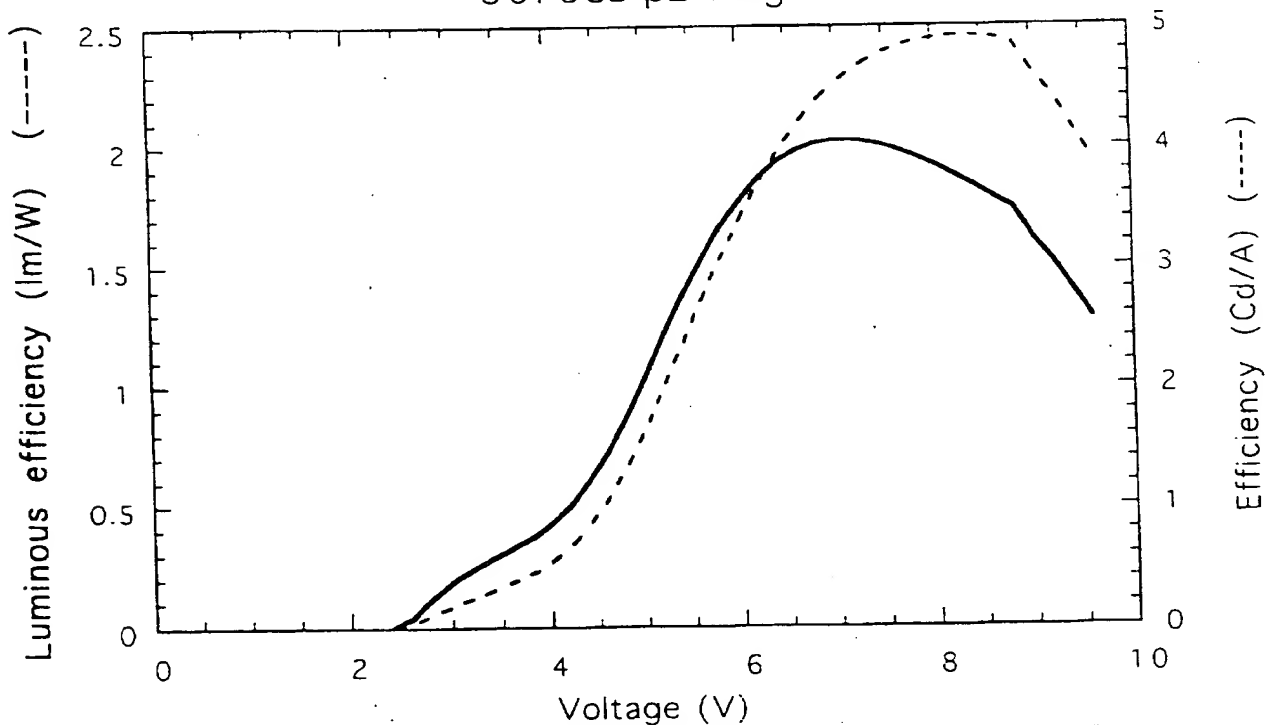
g.8

6/9

1:1.5 /5BTF8/Ca/Al 200C 5min air



5670CB p2 DRig



| SUMMARY DATA | | | | | |
|----------------------|--------|----------------------|--------|-----------------------|--------|
| Lumens/W @ 60 mA/sq | 1.3006 | Cd/A @ 60 mA/sq | 3.9591 | Final lm/W | 1.2774 |
| Max lm/W | 2.0262 | Max Cd/A | 4.9128 | Final Cd/A | 3.9054 |
| L(Cd/sqm)@max lm | 817.67 | L(Cd/sqm)@max Cd/A | 1901.2 | Final Light (Cd/sqm) | 2373.7 |
| I (mA/sq cm) @max lm | 18.102 | I (mA/sq cm) @max Cd | 38.700 | Final Current (mA/sq) | 60.780 |
| Volts (V)@max lm | 7.0000 | Volts (V)@max Cd/A | 8.4000 | Final Voltage (V) | 9.6000 |
| Volts (V)@ 0.01 Cd/s | 2.4501 | Volts (V)@ 30 Cd/Sqm | 4.4722 | Volts (V)@ 100 Cd/Sq | 5.1338 |

7/9

Fig. 9

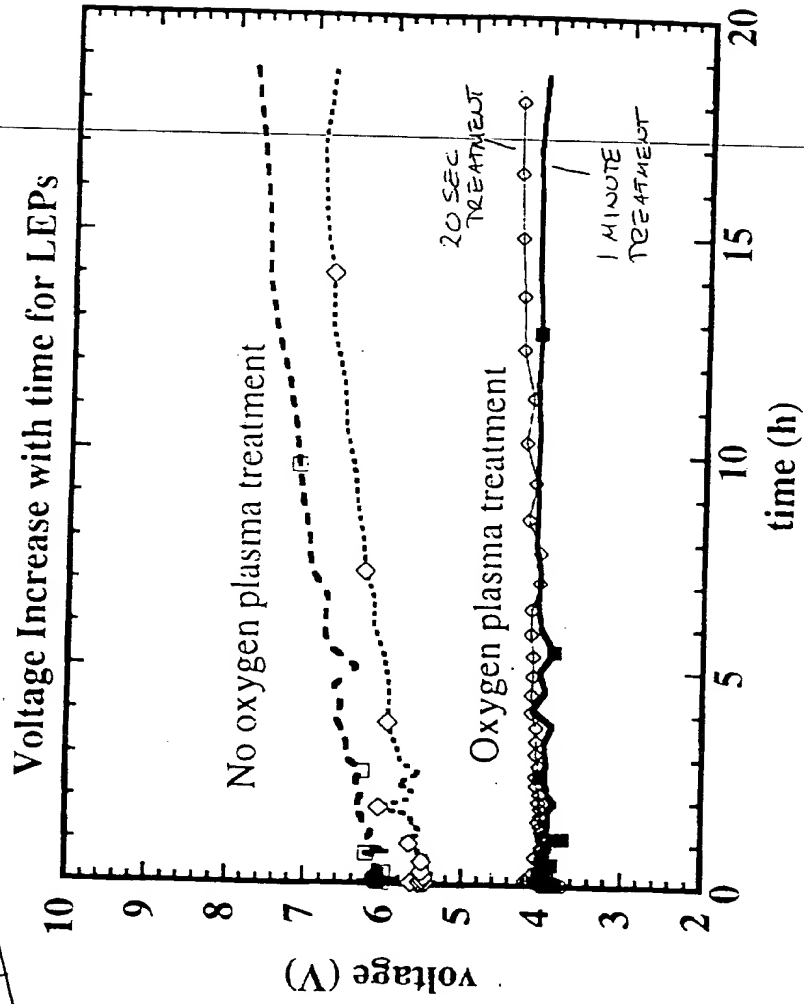
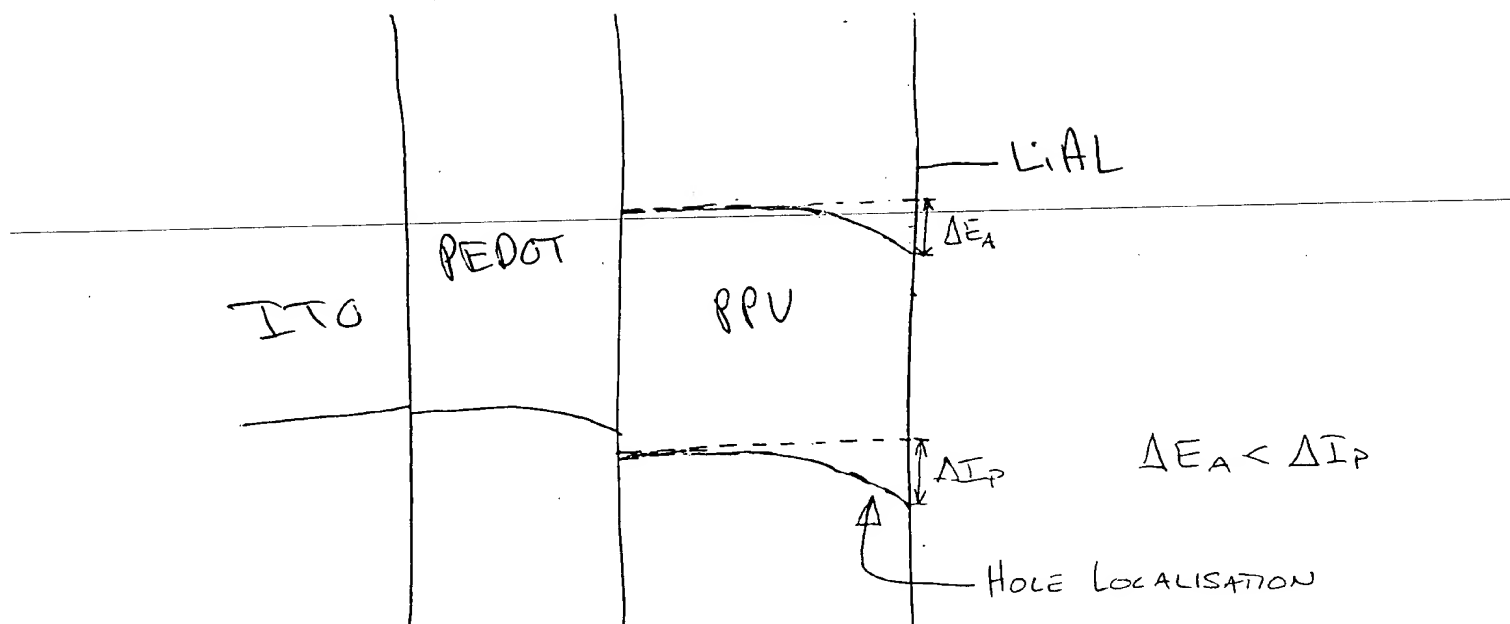


Figure 10

3/a



9/9

PPV AS HOLE INJECTOR

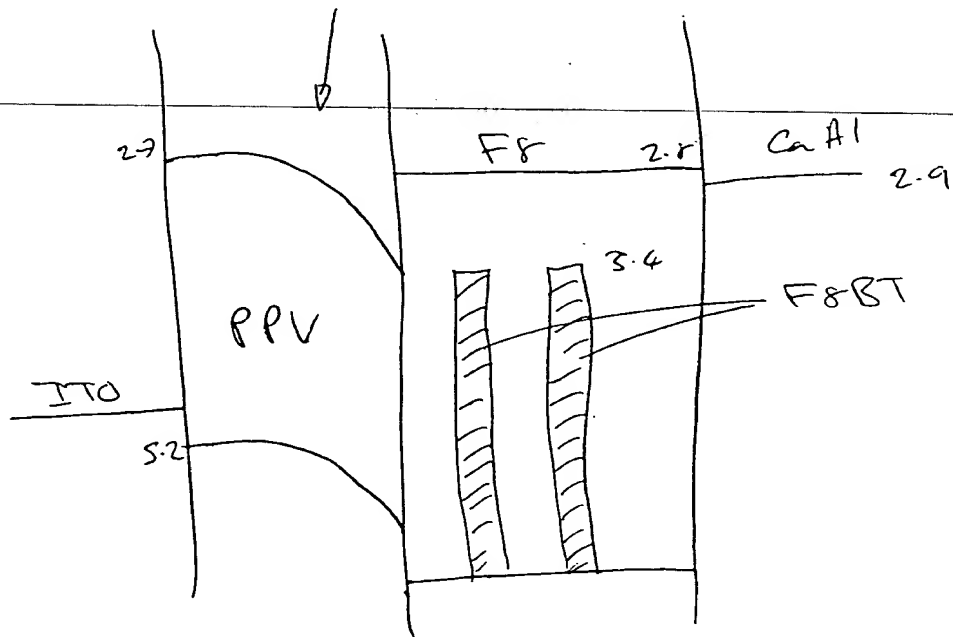


Figure 11

THIS PAGE BLANK (USPTO)